

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
31 December 2003 (31.12.2003)

PCT

(10) International Publication Number
WO 2004/001881 A2

- (15) International Patent Classification⁷: **H01M 4/58**
- (21) International Application Number:
PCT/EP2003/006628
- (22) International Filing Date: 19 June 2003 (19.06.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
02291562.3 21 June 2002 (21.06.2002) EP
60/392,978 2 July 2002 (02.07.2002) US
- (71) Applicants (*for all designated States except US*): UMICORE [BE/BE]; Rue du Marais 31, B-1000 Brussels (BE). LE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE [FR/FR]; 3, Rue Michel Ange, F-75794 Paris Cedex 16 (FR).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): AUDEMER, Albane [FR/BE]; Kasteelstraat 7, B-2250 Olen (BE). WURM, Calin [FR/FR]; 3, rue Michel Ange, F-75794 Paris Cedex 16 (FR). MORCRETTE, Mathieu [FR/FR]; 3, rue Michel Ange, F-75794 Paris Cedex 16 (FR). GWIZDALA, Sylvaln [FR/FR]; 3, rue Michel Ange, F-75794 Paris Cedex 16 (FR). MASQUELIER, Christian [FR/FR]; 3, rue Michel Ange, F-75794 Paris Cedex 16 (FR).
- (74) Common Representative: PILATE, André; Umicore - Patent Department, Kasteelstraat 7, B-2250 Olen (BE).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Declaration under Rule 4.17:**
— *of inventorship (Rule 4.17(iv)) for US only*
- Published:**
— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: CARBON-COATED LI-CONTAINING POWDERS AND PROCESS FOR PRODUCTION THEREOF

(57) Abstract: The invention provides a new route for the synthesis of carbon-coated powders having the olivine or NASICON structure, which form promising classes of active products for the manufacture of rechargeable lithium batteries. Carbon-coating of the powder particles is necessary to achieve good performances because of the rather poor electronic conductivity of said structures. For the preparation of coated LiFePO₄, sources of Li, Fe and phosphate are dissolved in an aqueous solution together with a polycarboxylic acid and a polyhydric alcohol. Upon water evaporation, polyesterification occurs while a mixed precipitate is formed containing Li, Fe and phosphate. The resin-encapsulated mixture is then heat treated at 700 °C in a reducing atmosphere. This results in the production of a fine powder consisting of an olivine LiFePO₄ phase, coated with conductive carbon. When this powder is used as active material in a lithium insertion-type electrode, fast charge and discharge rates are obtained at room temperature and an excellent capacity retention is observed.

Carbon-coated Li-containing powders and process for production thereof

- The present invention relates to the field of rechargeable lithium batteries and to positive electrode materials operating at voltages greater than 2.8 V vs. Li^+ / Li in non-aqueous electrochemical cells. This invention relates in particular to the use of phosphates or sulphates of transition metals as positive electrodes and allows the manufacturing of powdered Li-containing olivine-like and NASICON-like material, with the particles efficiently coated with a controlled amount of conductive carbon.
- 10 Lithium secondary batteries are now widely used in consumer electronics. They benefit from the light weight of Li and from its strong reducing character, thus providing the highest power and energy density among known rechargeable battery systems. Lithium secondary batteries are of various configurations depending on the nature of the electrode materials and of the electrolyte used. The commercialised Li-ion system, for instance, uses LiCoO_2 and Carbon
- 15 graphite as positive and negative electrodes, respectively with LiPF_6 in EC/DEC/PC as a liquid electrolyte. The operating voltage of the battery is related to the difference between thermodynamic free energies within the negative and positive electrodes. Solid oxidants are therefore required at the positive electrode, the materials of choice, up to now, being either the layered LiMO_2 oxides (with M is Co or Ni) or the 3-dimensional spinel structure of
- 20 $\text{Li}[\text{Mn}_2]\text{O}_4$. Extraction of Li from each of these three oxides gives access to $\text{M}^{4+} / \text{M}^{3+}$ redox couples located between 3.5 to 5 V vs. Li^+ / Li .

Three-dimensional framework structures using $(\text{XO}_4)^n$ polyanions have been proposed recently (US 5,910,382) as viable alternatives to the LiM_xO_y oxides. LiFePO_4 and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$

25 in particular are the most promising Fe-containing materials that can work at attractive potentials vs. Li^+ / Li (3.5 V and 2.8 V respectively). Both compounds operate on the $\text{Fe}^{3+} / \text{Fe}^{2+}$ redox couple which take advantage from the inductive effect of the XO_4^n groups that diminishes the strength of the Fe-O bond compared to a simple oxide.

- 30 Pioneering work by Padhi (Padhi et al., *J. Elec. Soc.* 144(4)) demonstrated the reversible extraction of Li from the olivine-structured LiFePO_4 prepared by solid state reaction at 800 °C under Ar atmosphere, starting from Li_2CO_3 or $\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{Fe}(\text{CH}_3\text{COO})_2$ and $\text{NH}_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. Unfortunately, probably due to kinetic limitations of the displacement of the $\text{LiFePO}_4 / \text{FePO}_4$ interface, only 60-70 % of the theoretical capacity of 170 mAh / g of active material, was
- 35 achieved, whatever the charge or discharge rate applied. Indeed, the use of high synthesis temperatures leads to the formation of large particles in which ionic and electronic

CONFIRMATION COPY

conductivity is the limiting factor. Several research groups recently reported improvements in the effective reversible capacity of LiFePO_4 by decreasing the particle size. This can be done by using highly reactive Fe^{II} precursors (JP 2000-294238 A2), or by using a solution route (WO 02 / 27824 A1), thus allowing LiFePO_4 formation at lower temperatures compared to the solid state route described by Padhi.

The poor electronic conductivity of the product can be improved by coating the particles with conductive carbon. This has been done by ball milling LiFePO_4 and carbon (Huang et al., *Electrochem. Solid-State Lett.*, 4, A170 (2001)) or by adding a carbon containing compound to already made LiFePO_4 and proceeding to a subsequent calcination at about 700 °C (CA 2,270,771). Carbon, and preferably amorphous carbon, can also be introduced in the LiFePO_4 synthesis process, being mixed with the solid synthesis precursors before calcination (EP 1184920 A2).

The main problems that may jeopardise the effective use in a positive electrode for Li batteries of Li-containing olivine or NASICON powders such as LiFePO_4 or other components mentioned by Goodenough et al. in US5,910,382, arises from their low electronic conductivity and from the fact that both end-members of the de-intercalation process (e.g. LiFePO_4 and FePO_4) are poor ionic conductors.

As described above, adding carbon, thereby coating the particles with a conductive layer, alleviates the electronic conductivity problem. However, high amounts of carbon are needed. Whereas carbon does not participate in the redox reactions useful for the operation of the battery, a strong penalty for the overall specific capacity of the composite positive electrode is paid. This is illustrated in JP 2000-294238 A2 wherein a LiFePO_4 / Acetylene Black ratio of 70 / 25 is used.

The ionic conduction problem can be solved by producing very fine-grained particles. Using a solution route synthesis has been found to be advantageous compared to the classic solid synthesis route. This solution route has been described in EP1261050. This route provides for a very finely divided, homogeneous precursor which needs only moderate conditions of temperature and time to react to the desired crystalline structures. Thanks to the moderate conditions, grain growth, leading to unwanted coarse particles, is avoided. After synthesis, such a powder has to be ball-milled with a relatively large quantity of conductive carbon, typically amounting to 17 wt. % .

This invention provides for an improved solution route, ensuring the production of fine grained particles efficiently covered with a conductive carbon layer. Compared to prior art powders, the obtained powders deliver exceptional performances when used in Li-ion batteries. The invention provides for a powder that needs much less total carbon in the electrode for a similar electrode capacity and discharge rate. Similarly, the invention provides for a powder that provides higher capacity and discharge rate when using the same amount of total carbon in the electrode.

A new process is presented for preparing a carbon-coated Li-containing olivine or NASICON powder, comprising the steps of

- preparing a water-based solution comprising, as solutes, one or more Li-containing olivine or NASICON precursor compounds and one or more carbon-bearing monomer compounds,
- precipitating a Li-containing olivine or NASICON precursor compounds and polymerising the monomer compounds in a single step,
- heat treating the obtained precipitate in a neutral or reducing environment so as to form a Li-containing olivine or NASICON crystalline phase and decompose the polymer carbon.

The process is specially suitable for the preparation of $\text{Li}_u\text{M}_v(\text{XO}_4)_w$ with $u = 1, 2$ or 3 , $v = 1$ or 2 , $w = 1$ or 3 , M is $\text{Ti}_a\text{V}_b\text{Cr}_c\text{Mn}_d\text{Fe}_e\text{Co}_f\text{Ni}_g\text{Sc}_h\text{Nb}_i$ with $a+b+c+d+e+f+g+h+i = 1$ and X is P_{x-1}S_x with $0 \leq x \leq 1$.

It is clear that the individual 'a' to 'i' parameters have values going from 0 to 1. Obviously, their particular values should allow for electroneutrality of the crystalline phase when combined with a proper set 'u', 'v' and 'w' parameters. Examples are: LiMPO_4 such as in LiFePO_4 , LiNiPO_4 , LiMnPO_4 ; $\text{LiM}_2(\text{PO}_4)_3$ such as in $\text{LiTi}_2(\text{PO}_4)_3$, $\text{LiFeNb}(\text{PO}_4)_3$; $\text{Li}_2\text{M}_2(\text{PO}_4)_3$ such as in $\text{Li}_2\text{FeTi}(\text{PO}_4)_3$; $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ such as in $\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$, $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$, $\text{Li}_3\text{In}_2(\text{PO}_4)_3$, $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$, $\text{Li}_3\text{FeV}(\text{PO}_4)_3$.

The invented process is especially suitable for the preparation of coated LiFePO_4 .

The precipitation of Li-containing olivine or NASICON precursor compounds and the polymerisation of the monomers can be performed by evaporating water from the water-based solution. The carbon-bearing monomer compounds can be a polyhydric alcohol and a polycarboxylic acid, such as, respectively, ethylene glycol and citric acid.

When the synthesis of coated LiFePO_4 , is envisaged, equimolar amounts of Li, Fe and phosphate, such as LiH_2PO_4 and $\text{Fe}(\text{NO}_3)_3$, are dissolved in water together with a polyhydric alcohol and a polycarboxylic acid, the water is then evaporated at a temperature between 60 and 100 °C, and a heat-treatment is performed at a temperature between 600 and 800 °C, preferably between 650 and 750 °C.

The object of the invention also concerns a carbon-coated LiFePO_4 powder for use in Li insertion-type electrodes, which, when used as an active component in a cathode cycled between 2.0 and 4.5 V against a Li anode at a discharge rate of C / 5 at 25 °C, is characterised by a reversible electrode capacity expressed as a fraction of the theoretical capacity and a total carbon content of at least 75 % capacity and less than 4 wt. % carbon, or, at least 80 % capacity and less than 8 wt. % carbon.

Other objects of the invention are: an electrode mix containing the above-mentioned carbon-coated LiFePO_4 and batteries containing the latter electrode mix.

For a proper understanding of the invention as described herein, the following definitions are to be considered.

A "Li-containing olivine or NASICON precursor compound" is to be understood as a metal-bearing compound such as a salt, oxide or hydroxide of one or more metals susceptible to be converted to, or to react to, the desired final compound. Typically, the conversion or reaction is performed by applying a thermal treatment.

A "carbon-bearing monomer compound" is to be understood as an organic compound susceptible to polymerise with itself (to form a homopolymer) or together with other monomers (to form a copolymer).

A "reducing environment" can be obtained by using a reducing gas, or by relying on reducing properties of solids, such as carbon, present in the bulk of the material.

The "electrode capacity expressed as a fraction of the theoretical capacity" is the ratio of the capacity of the active product contained in the electrode, to the theoretical capacity of the active product. For FeLiPO_4 , a specific theoretical capacity of 170 mA / g is assumed.

When the charge or discharge rate is expressed as C / x , this means that one Li per LiFePO_4 is exchanged in 'x' hour.

- 5 The general principle of the invention can be applied whenever a high quality carbon coating is needed on a metal-bearing powder. Olivine and NASICON phases, when used in rechargeable Li-ion batteries, are known to be rather poor electronic conductors. As such, they particularly benefit from a carbon coating which is rendered conductive by a suitable heat treatment.
- 10 It is assumed that the metal bearing precursors, such as Li, metal and phosphate or sulphate ions, are trapped homogeneously on the atomic scale throughout the chelating polymer matrix. Such a structure eliminates the needs for long range diffusion during the subsequent formation of the crystalline phase. Therefore, at relatively low temperature, the precursors can form a homogeneous single phase of precise stoichiometry, intimately coated by a conductive
- 15 carbonaceous network.

Solvent evaporation conducting to an homogeneous mix of solid precursor compounds and the polymerisation of the monomers are performed in one single step. This requires the polymerisation to occur simultaneously with the solidification of at least part of the precursor.

20

- Different means can be employed to form the homogeneous mix of precursor (e.g. change in pH, temperature) and to trigger the polymerisation (e.g. addition of catalyst, UV). However, when the polymerisation reaction produces water as a condensate, both the precipitation of the precursor and the polymerisation are triggered by identical means, i.e. by removal of water
- 25 from the reaction vessel. This results in a particularly simple and efficient process.

- It has been found that the presence of heteroatoms (i.e. atoms other than C, O and H) in the monomers may degrade the performance of the obtained carbon coating, in particular its electrical conductivity. It is therefore preferred to use monomer compounds containing only C,
- 30 O and H atoms.

When the production of LiFePO_4 is envisaged, the Fe source in the precursor compound can be Fe^{II} or Fe^{III} : the reducing conditions needed to avoid the burning of the carbon coating during the step of heat treatment ensures the conversion of any Fe^{III} to the required Fe^{II} state.

35

The preferred water evaporation temperature range is 60 to 100 °C. This ensures that the precipitation of the precursor compound and the polymerisation reaction occur at least partly simultaneously.

- 5 The conductivity of the carbon residue is enhanced when the heat treatment is performed at 600 °C or higher. However, a temperature of more than 800 °C may degrade the quality of the product because of grain-growth or because of excessive reduction by carbon. A heat treatment at 650 to 750 °C is preferred.
- 10 The positive electrode of the electrochemical cell is made of optimised LiFePO_4 particles intimately mixed with an electronically conducting carbon species made as described below. The active material / coated-carbon ratio can be adjusted in the synthesis of LiFePO_4 between 1 and 25 wt. % of carbon. It is preferred to minimise the relative amount of carbon, whether present as coating material or as carbon added during the manufacture of the electrode. Indeed,
- 15 carbon does not participate in the redox reactions and therefore represents inert mass reducing the specific capacity of the electrode. Nevertheless, it is desired to have at least 2 wt. % of coated carbon to exploit the invention fully.

- 20 The invention is illustrated by the preparation of optimised LiMPO_4 particles, coated with (electronic) conductive carbon through low-temperature chemical routes.

- For the preparation of a LiFePO_4 / C composite, an aqueous solution containing Fe, Li and phosphate is prepared using e.g. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and LiH_2PO_4 . The solution is added under stirring in air to an aqueous solution of citric acid. Ethylene glycol is then added to the solution
- 25 for an ethylene glycol / citric acid molar ratio of 1 / 1. The precursor to carbon ratio in the solution will determine the relative amount of carbon in the coating. Key to this process are the fact that both the LiFePO_4 precursors and the monomers are to be water-soluble.

- In a second step, the water is slowly evaporated at 80 °C under air. When nearly dry, the
- 30 solution turns to a gel due to the polymerisation between citric acid and ethylene glycol. The gel is dried by maintaining it at 80 °C. A very homogeneous mixture, containing Li, Fe and phosphate in the stoichiometric proportions of LiFePO_4 together with the carbon bearing polymer, is then produced. Advantageously, monomers are chosen which have a lower partial pressure than water at the drying temperature. Premature evaporation of the monomers is thus
- 35 avoided.

In a third step, the homogeneous mixture is progressively heat-treated under a reducing atmosphere (N_2/H_2 , 10 % H_2) to yield, at a temperature of about 500 °C, a crystalline $LiFePO_4$ phase coated with a controlled amounts coated carbon. However, at 500 °C, the coated carbon is partly insulating. A treatment between 600 °C and 800 °C is thus preferred as it yields

5 conductive carbon. Thanks to the presence of carbon, the surrounding environment of $LiFePO_4$ is strongly reducing. This is useful to reduce remaining traces of Fe^{III} precursors to Fe^{II} , but can lead to unwanted results when the percentage of carbon is high. Indeed, high carbon contents (more than 15 %) combined with prolonged treatment (more than 5 hours) at 700 to 800 °C partly reduces Fe^{II} in $LiFePO_4$ to Fe^0 . This leads to the formation of impurities such as

10 Fe_2P . As determined by electrochemical titration, the obtained optimised powder may still contain a small amount of Fe^{III} (less than 3 M%), an amount which is in fact inferior to that obtained in the synthesis of pure $LiFePO_4$ without carbon. The result of the heat treatment can easily be monitored and optimised by e.g. X-ray diffraction or by Mossbauer spectroscopy, to ensure that Fe^{III} is nearly completely reduced to Fe^{II} and that no significant amount of Fe^{II} is

15 reduced to Fe^0 .

The invention is illustrated by the following examples. Four $LiFePO_4/C$ composites were produced according to the process described above. Aqueous solutions containing 0.4 M / l Fe, Li and phosphate and 0.1 to 1 M / l ethylene glycol and citric acid were prepared using

20 $Fe(NO_3)_3 \cdot 9H_2O$ and LiH_2PO_4 . The solutions were dried for 12 h at 80 °C. The dry residues were then heat treated for 10 h at 700 °C under a N_2/H_2 atmosphere with 10 % H_2 .

The results, presented in Table 1, show the influence of the monomer concentrations in the solution on the amount of carbon coated on the $LiFePO_4$ particles. The apparent loss of carbon,

25 which is rather high compared to the theoretical amount expected, comes probably from the reduction of Fe^{III} to Fe^{II} during the heat treatment. The polymerisation needs not be complete.

30

35

Table 1: Theoretical vs. observed amount of carbon in the coating as a function of the monomer concentration in the solute (for 0.1 M / l of Fe, Li and phosphate in the solute)

Citric acid (M / l)	Ethylene glycol (M / l)	Theoretical C (wt.%)	Observed C (wt.%)
0.1	0.1	13.2	0.33
0.2	0.2	23.3	3.6
0.4	0.4	37.8	8.6
1	1	60.3	24

5

Figures 1 to 5 illustrate the invention.

Fig. 1: X-ray diffractograms ($\text{CuK}\alpha$) and the S.E.M. photographs of two LiFePO_4 powders coated with 3.6 (top) and 24 % (bottom) carbon

10

Fig. 2: Electrochemical response of a $\text{Li} / \text{LiPF}_6 \text{ EC:DMC} / \text{LiFePO}_4$ electrochemical cell (swagelok type) cycled at C / 5 and 25 °C, using LiFePO_4 with 3.6 (top) and 24 % (bottom) of coated carbon

15

Fig. 3: Results obtained with $\text{Li} / \text{LiPF}_6 \text{ EC : DMC} / \text{LiFePO}_4$ electrochemical coin cells embedded in a plastic film. LiFePO_4 with 3.6 % of coated carbon cycled at C / 5 and 25 °C (A) or 55 °C (B); LiFePO_4 prepared according to the prior art solution route and ball-milled with 17 % of conductive carbon cycled at C / 10 and 55 °C (C)

20

Fig. 4: In situ XRD patterns of LiFePO_4 in a $\text{Li} / \text{LiPF}_6 \text{ EC : DMC} / \text{LiFePO}_4$ electrochemical cell cycled at C / 5 and 25 °C; LiFePO_4 prepared according to the invention (top) and according to the prior art solution route and ball-milled with 17 % of conductive carbon (bottom)

25

Fig. 5: Evolution of the specific active material capacity achieved in a $\text{Li} / \text{LiPF}_6 \text{ EC : DMC} / \text{LiFePO}_4$ prepared according to the invention with 3.6 (B) and 24 % (C) of coated carbon; LiFePO_4 prepared according to the prior the art solution route and ball-milled with 17 % of conductive carbon (D); commercial LiCoO_2 are shown for comparison (A)

Figures 1 to 5 are now discussed in more details. The X-ray diffractograms and the S.E.M. photographs of two LiFePO_4 powders coated with 3.6 and 24 % of carbon are given in Figure 1. The photographs are representative for the overall powder. For LiFePO_4 with 3.6 % of coated carbon, the network formed by the coated particles is very well spaced and regular. The particles are sufficiently fine (around 1 μm) to alleviate the penalising displacement length of the interface between LiFePO_4 and FePO_4 , while enough space is left for species to migrate. For 24 % of coated carbon, the carbon matrix itself can be observed. The carbon network surrounds the LiFePO_4 particles whose size is even smaller than in the former case. The LiFePO_4 phase appears to be pure when 3.6 % of carbon is coated. When 24 % is coated, some LiFePO_4 is reduced to Fe_2P after 10 h at 700 °C. This demonstrates that the higher the carbon percentage, the more efficient the reduction.

These powders give the electrochemical response shown in Figure 2. The electrochemical cells were built in Swagelok configuration with Li metal pasted on a Ni foil as the negative electrode, and LiPF_6 in EC : DMC as the electrolyte. The positive electrode is the powder obtained directly from the described process. The signature of Figure 2 (voltage as a function of x in Li_xFePO_4) was obtained at 25 °C for an equivalent charge / discharge rate of C / 5, i.e. 1 Li extracted or inserted in 5 h.

About 85 % of the theoretical capacity of the active material can be achieved when using 24 % of coated carbon. The performance of the total electrode is however rather penalised by the large quantity of carbon. The amount of carbon can be dramatically decreased. When using 3.6 % of coated carbon, 78 % of the capacity is still achieved. In each case, the irreversible capacity at first cycle is very small.

Figure 3 illustrates the stability of the LiFePO_4 composite produced according to the invention using 3.6 % of coated carbon. This material was cycled at C / 5 at 25 and at 55 °C. The resulting specific capacity is superior to that obtained with uncoated material prepared according to the prior art solution route and ball-milled with 17 % of conductive carbon. If we compare the specific capacities of the total electrodes, the superiority of the invented process becomes even more apparent thanks to the much lower amount of total carbon.

In Figure 4, in situ X-ray diffraction patterns are shown for a full charge / discharge cycle. With the powder coated according to the invention, at the end of the charge cycle, all the diffraction peaks of LiFePO_4 disappear at the benefit of triphylite- FePO_4 peaks. The biphasic

phenomenon is thus complete. However, with powder prepared according to the prior art solution route, this is not the case.

- 5 In Figure 5, the specific capacity of several active materials is reported in function of the cycling rate. Materials tested are: LiFePO_4 composite obtained by the process according to the invention with 3.6 and 24 % of coated carbon, LiFePO_4 prepared according to the prior art solution route and ball-milled with 17 % of conductive carbon, and commercial LiCoO_2 . The 3.6 % carbon-coated LiFePO_4 performs better than any other at low discharge rates. At higher
- 10 rates, it is outperformed by LiCoO_2 (a much more expensive product), and, as expected, by 24 % carbon-coated LiFePO_4 . Indeed, the higher amount of coated carbon tends to improve the high current performance. Whatever the conditions, however, the products which are carbon-coated according to the invention remain superior to the prior art product.

Claims

1. Process for preparing a carbon-coated, Li-containing olivine or NASICON powder, comprising the steps of
- 5 - preparing a water-based solution comprising, as solutes, one or more Li-containing olivine or NASICON precursor compounds and one or more carbon-bearing monomer compounds,
- precipitating the Li-containing olivine or NASICON precursor compounds and polymerising the monomer compounds in a single step
- heat treating the obtained precipitate in a neutral or reducing environment so as to form a Li-
- 10 containing olivine or NASICON crystalline phase and decompose the polymer to carbon.
2. Process according to claim 1, whereby the crystalline phase is $\text{Li}_u\text{M}_v(\text{XO}_4)_w$ with $u = 1, 2$ or 3 , $v = 1$ or 2 , $w = 1$ or 3 , M is $\text{Ti}_a\text{V}_b\text{Cr}_c\text{Mn}_d\text{Fe}_e\text{Co}_f\text{Ni}_g\text{Sc}_h\text{Nb}_i$ with $a+b+c+d+e+f+g+h+i = 1$ and X is P_{x-1}S_x with $0 \leq x \leq 1$
- 15
3. Process according to claim 2, whereby the crystalline phase is LiFePO_4
4. Process according to claim 1, whereby the precipitation of Li-containing olivine or NASICON compounds and the polymerisation of the monomers is performed by evaporating
- 20 water from the water-based solution
5. Process according to claim 4, whereby the carbon-bearing monomer compounds are a polyhydric alcohol and a polycarboxylic acid
- 25
6. Process according to claim 5, whereby the polyhydric alcohol is ethylene glycol and the polycarboxylic acid is citric acid
7. Process for the production of carbon-coated LiFePO_4 according to claim 5, whereby
- 30 - the water-based solution contains equimolar amounts of Li, Fe and phosphate,
- the evaporation of water from the solution is performed at a temperature between 60 and 100 °C,
- the heat-treatment is performed at a temperature between 600 and 800 °C, preferably between 650 and 750 °C

8. Process according to claim 7 whereby the water-based solution is prepared using LiH_2PO_4 and $\text{Fe}(\text{NO}_3)_3\cdot\text{aq}$

5 9. A carbon-coated LiFePO_4 powder for use in Li insertion-type electrodes, which, when used as an active component in a cathode cycled between 2.0 and 4.5 V against a Li anode at a discharge rate of C / 5 at 25 °C, is characterised by a reversible electrode capacity expressed as a fraction of the theoretical capacity and a total carbon content of at least 75 % capacity and less than 4 wt.% carbon, or, at least 80 % capacity and less than 8 wt.% carbon.

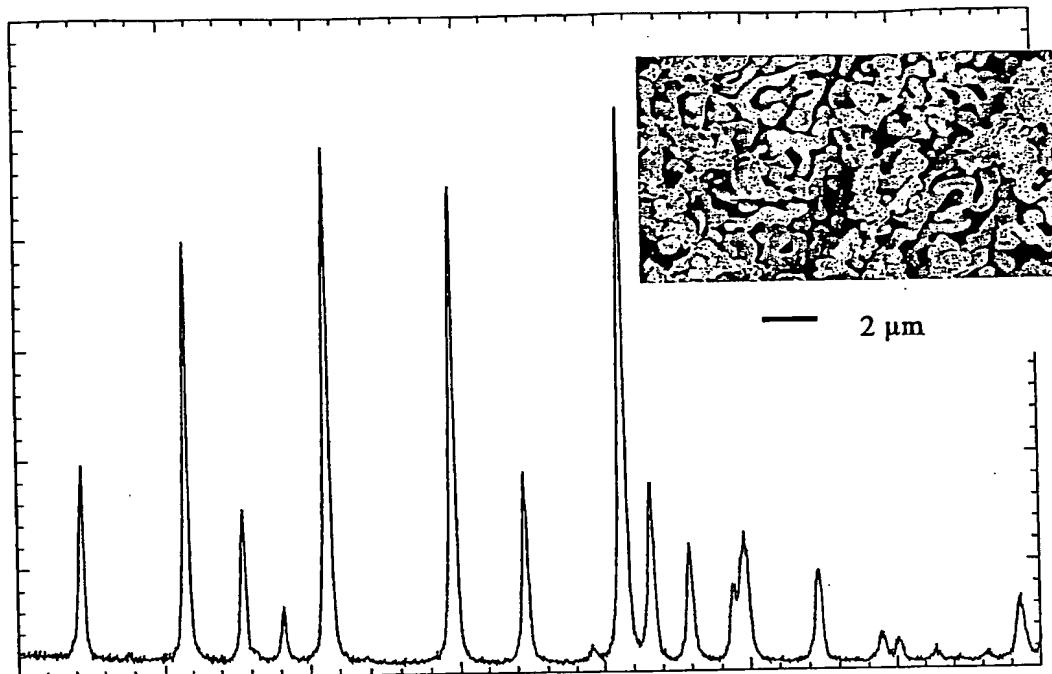
10

10. Electrode mix containing carbon-coated LiFePO_4 according to claim 9

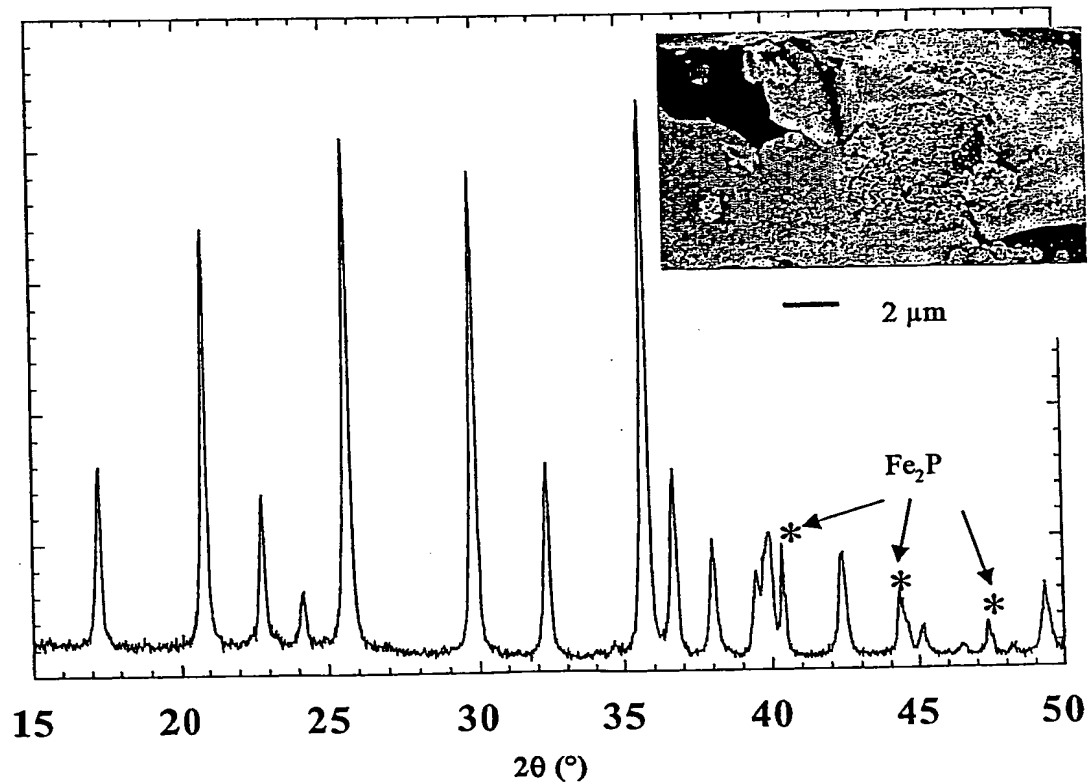
11. A battery containing an electrode mix according to claims 10

1/5

I

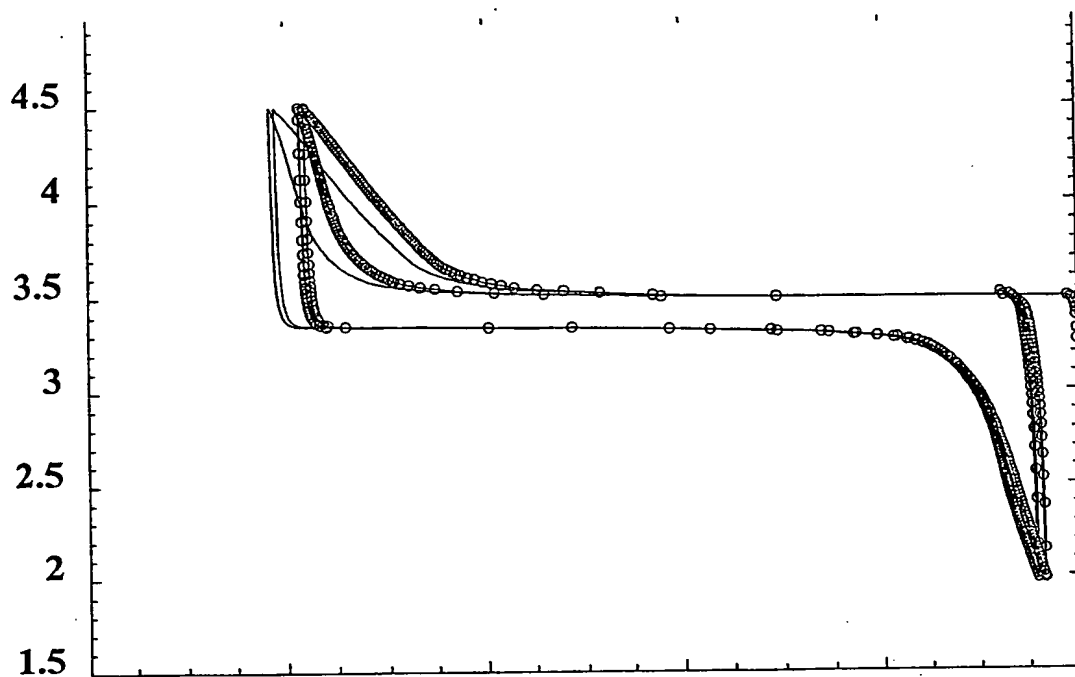
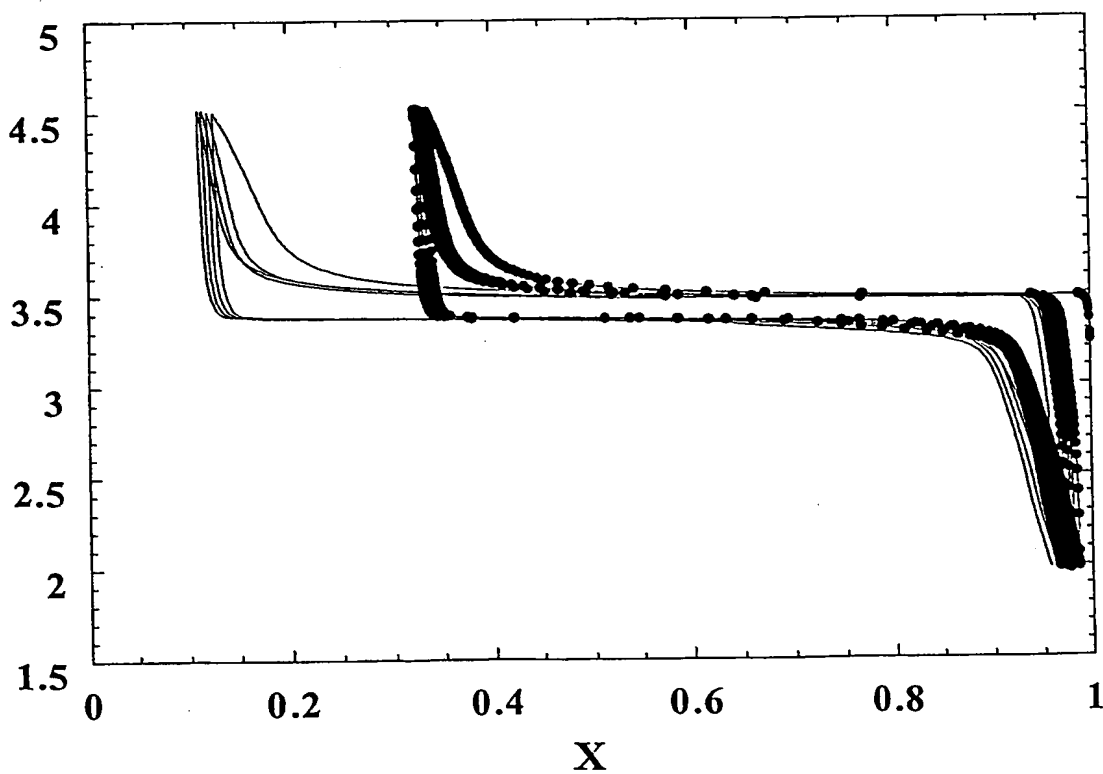


I

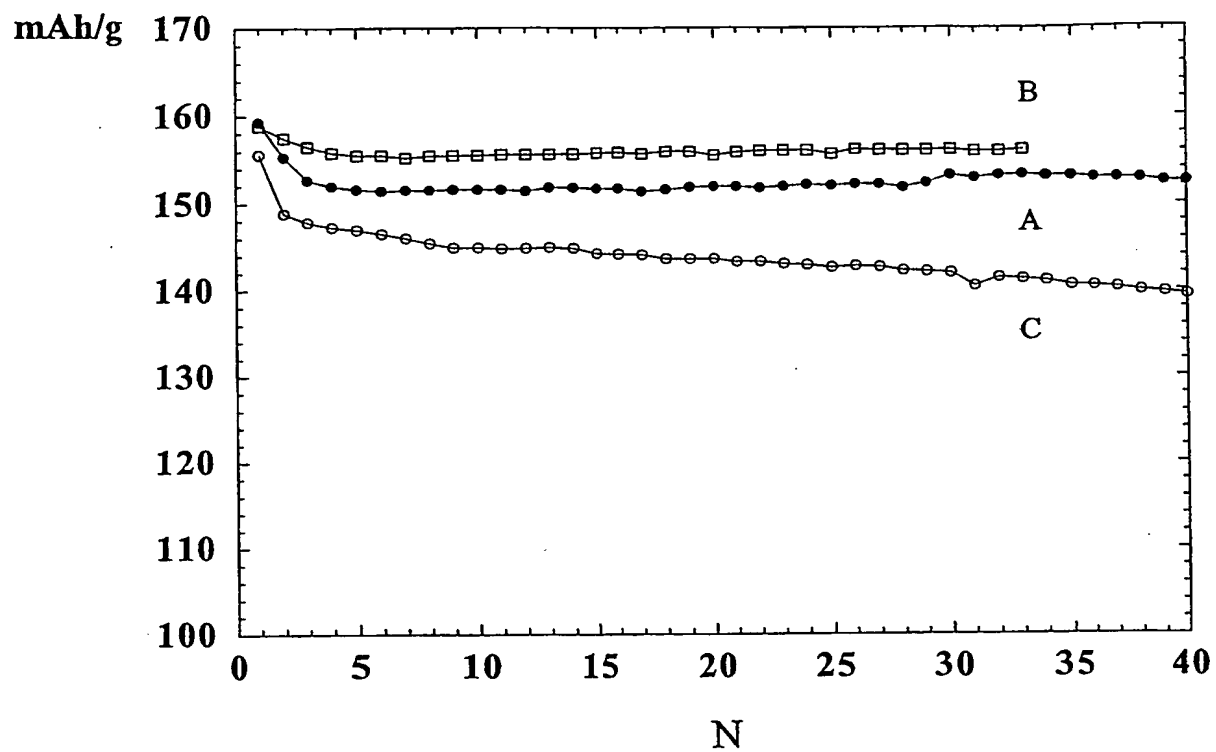
**Figure 1**

CONFIRMATION COPY

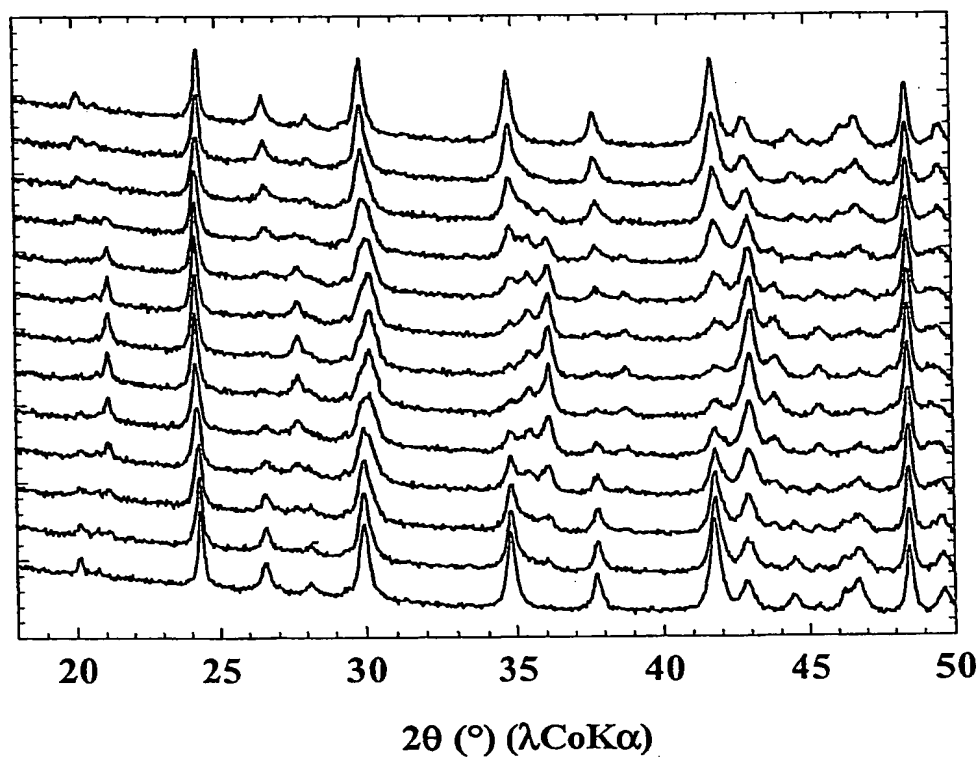
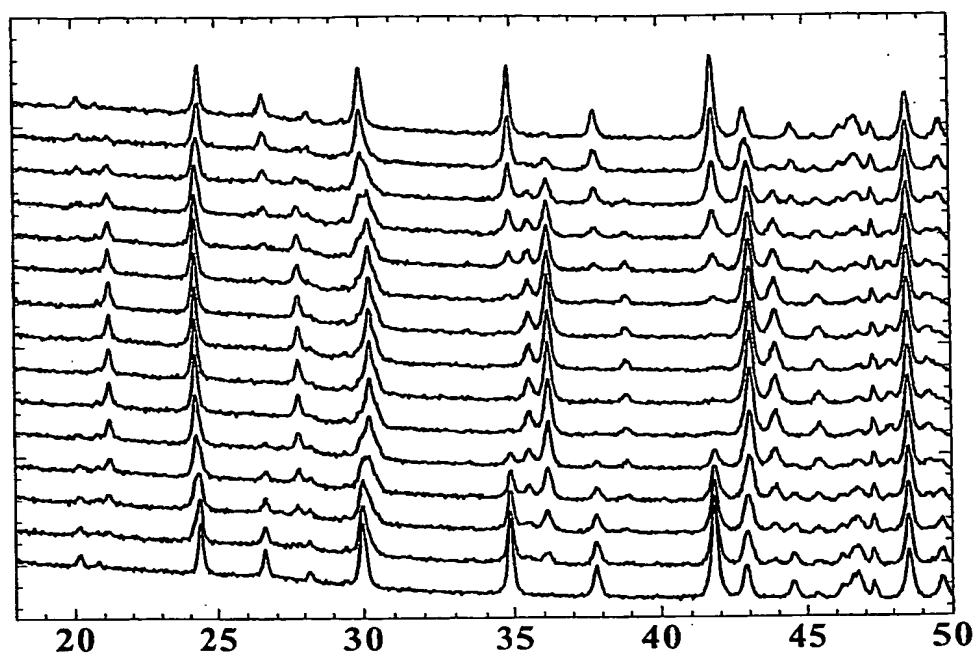
2/5

 V
 Li^+/Li  V
 Li^+/Li Figure 2

CONFIRMATION COPY

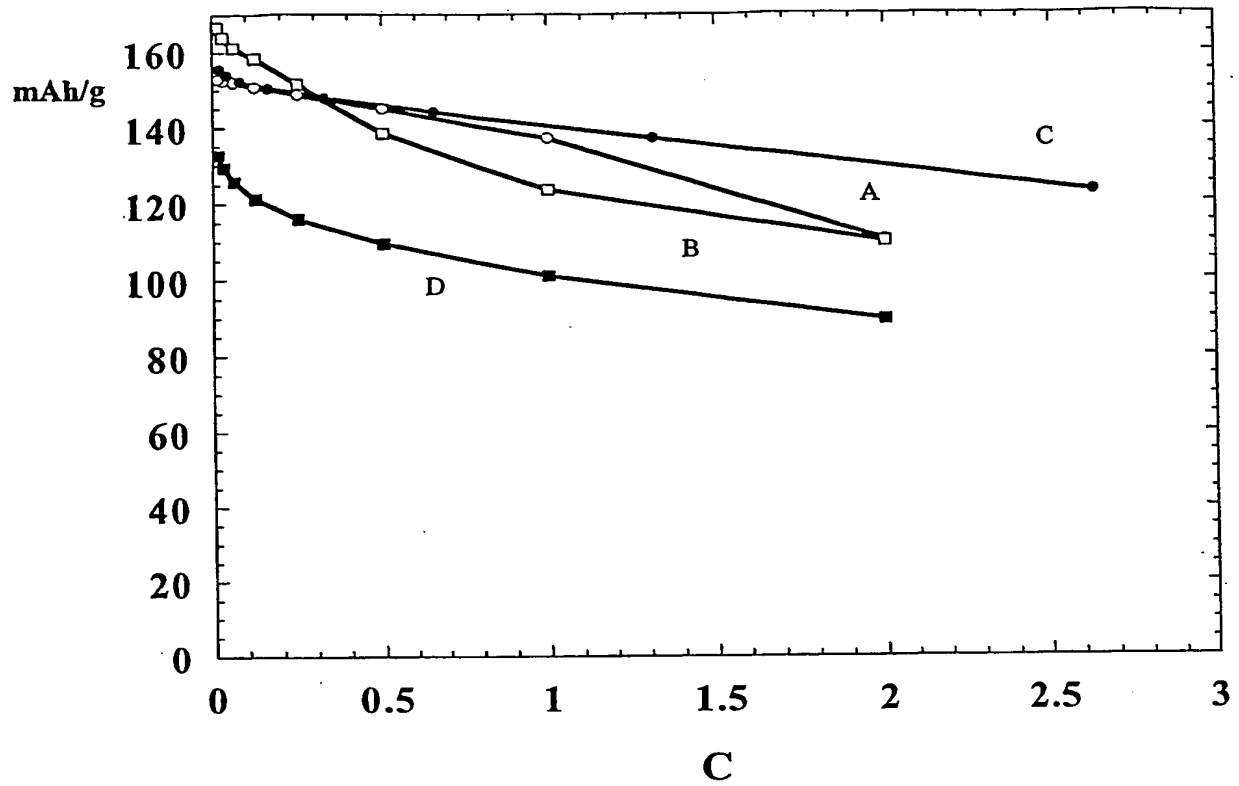
**Figure 3**

4/5

**Figure 4**

CONFIRMATION COPY

5/5

**Figure 5**

CONFIRMATION COPY

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
31 December 2003 (31.12.2003)

PCT

(10) International Publication Number
WO 2004/001881 A3

(51) International Patent Classification⁷: **H01M 4/58**,
C09C 3/10, C01B 25/30, H01M 4/62, 4/36

(21) International Application Number:
PCT/EP2003/006628

(22) International Filing Date: 19 June 2003 (19.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02291562.3 21 June 2002 (21.06.2002) EP
60/392,978 2 July 2002 (02.07.2002) US

(71) Applicants (for all designated States except US): **UMI-CORE** [BE/BE]; Rue du Marais 31, B-1000 Brussels (BE). **LE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE** [FR/FR]; 3, Rue Michel Ange, F-75794 Paris Cedex 16 (FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **AUDEMER**, Albane [FR/BE]; Tramweglei 31, B-2500 Lier (BE). **WURM**, Calin [FR/FR]; 18 rue Marc Sangnier, F-80000 Amiens (FR). **MORCRETTE**, Mathieu [FR/FR]; 130 rue Vulfran Warmé, F-80000 Amiens (FR). **GWIZDALA**, Sylvain [FR/FR]; 8 rue Charles Bazile, F-89210 Brienon sur Armançon (FR). **MASQUELIER**, Christian [FR/FR]; 282 Bvd. deBeauvillé, F-80000 Amiens (FR).

(74) Common Representative: **PILATE**, André; Umicore - Patent Department, Kasteelstraat 7, B-2250 Olen (BE).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
29 December 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CARBON-COATED LI-CONTAINING POWDERS AND PROCESS FOR PRODUCTION THEREOF

(57) Abstract: The invention provides a new route for the synthesis of carbon-coated powders having the olivine or NASICON structure, which form promising classes of active products for the manufacture of rechargeable lithium batteries. Carbon-coating of the powder particles is necessary to achieve good performances because of the rather poor electronic conductivity of said structures. For the preparation of coated LiFePO₄, sources of Li, Fe and phosphate are dissolved in an aqueous solution together with a polycarboxylic acid and a polyhydric alcohol. Upon water evaporation, polyesterification occurs while a mixed precipitate is formed containing Li, Fe and phosphate. The resin-encapsulated mixture is then heat treated at 700 °C in a reducing atmosphere. This results in the production of a fine powder consisting of an olivine LiFePO₄ phase, coated with conductive carbon. When this powder is used as active material in a lithium insertion-type electrode, fast charge and discharge rates are obtained at room temperature and an excellent capacity retention is observed.

WO 2004/001881 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06628

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M4/58 C09C3/10 C01B25/30 H01M4/62 H01M4/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M C09C C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/27823 A (ARMAND MICHEL ; GAUHTIER MICHEL (CA); HYDRO QUEBEC (CA); RAVET NATH) 4 April 2002 (2002-04-04) page 11, line 1 - line 13 page 12, line 7 - line 11 page 15, line 7 - line 11 page 16, line 4 - page 18, line 6 examples 2-5; table 2	9-11
A		1-8
X	EP 1 184 920 A (SONY CORP) 6 March 2002 (2002-03-06) cited in the application page 4, line 3 - line 25 page 5, line 48 - line 57 page 6, line 57 - page 7, line 7 tables 1,3,4	9-11
A		1-8
	----- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

11 November 2004

Date of mailing of the international search report

18/11/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Gamez, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06628

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2 320 661 A (HYDRO-QUEBEC) 26 March 2002 (2002-03-26) page 3, paragraph 3 page 4, paragraph 3 - page 5, paragraph 2	9-11
A	examples 2,3,5 -----	1-8
X	CA 2 270 771 A (HYDRO-QUEBEC) 30 October 2000 (2000-10-30) cited in the application page 4, line 1 - line 8 page 5, line 20 - page 7, line 1 page 8, line 14 - page 9, line 5 page 11, line 1 - line 5	9-11
A	-----	1-8
X	EP 1 193 787 A (SONY CORP) 3 April 2002 (2002-04-03) page 3, line 19 - line 36 page 4, line 24 - line 27 page 4, line 51 - page 5, line 2 page 7, line 39 - line 46 page 9, line 1 - line 5 table 1	9-11
A	-----	1-4,8
X	HUANG H ET AL: "APPROACHING THEORETICAL CAPACITY OF LIFEPO4 THE ROOM TEMPERATURE AT HIGH RATES" ELECTROCHEMICAL AND SOLID-STATE LETTERS, IEEE SERVICE CENTER, PISCATAWAY, NJ, US, vol. 4, no. 10, October 2001 (2001-10), pages A170-A172, XP001100987 ISSN: 1099-0062 the whole document	1-4,7-11
A	-----	
A	US 5 910 382 A (MASQUELIER CHRISTIAN ET AL) 8 June 1999 (1999-06-08) the whole document	1-11
P,A	-----	
P,A	EP 1 261 050 A (UMICORE S A NV ; CENTRE NAT RECH SCIENT (FR)) 27 November 2002 (2002-11-27) the whole document	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/06628

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0227823	A	04-04-2002	CA 2320661 A1	26-03-2002
			AU 9356801 A	08-04-2002
			AU 9356901 A	08-04-2002
			WO 0227823 A1	04-04-2002
			WO 0227824 A1	04-04-2002
			CA 2422446 A1	04-04-2002
			CA 2423129 A1	04-04-2002
			CN 1478310 T	25-02-2004
			EP 1325525 A1	09-07-2003
			EP 1325526 A1	09-07-2003
			JP 2004509447 T	25-03-2004
			JP 2004509058 T	25-03-2004
			US 2004033360 A1	19-02-2004
			US 2004086445 A1	06-05-2004
EP 1184920	A	06-03-2002	JP 2002075364 A	15-03-2002
			CN 1340869 A	20-03-2002
			EP 1184920 A2	06-03-2002
			TW 518785 B	21-01-2003
			US 2002047112 A1	25-04-2002
CA 2320661	A	26-03-2002	CA 2320661 A1	26-03-2002
			AU 9356801 A	08-04-2002
			AU 9356901 A	08-04-2002
			WO 0227823 A1	04-04-2002
			WO 0227824 A1	04-04-2002
			CA 2422446 A1	04-04-2002
			CA 2423129 A1	04-04-2002
			CN 1478310 T	25-02-2004
			EP 1325525 A1	09-07-2003
			EP 1325526 A1	09-07-2003
			JP 2004509447 T	25-03-2004
			JP 2004509058 T	25-03-2004
			US 2004033360 A1	19-02-2004
			US 2004086445 A1	06-05-2004
CA 2270771	A	30-10-2000	CA 2270771 A1	30-10-2000
			CA 2307119 A1	30-10-2000
			EP 1049182 A2	02-11-2000
			JP 2001015111 A	19-01-2001
			US 2002195591 A1	26-12-2002
			US 2004140458 A1	22-07-2004
EP 1193787	A	03-04-2002	JP 2002110161 A	12-04-2002
			CN 1350341 A	22-05-2002
			EP 1193787 A2	03-04-2002
			TW 518781 B	21-01-2003
			US 2002114754 A1	22-08-2002
US 5910382	A	08-06-1999	US 6391493 B1	21-05-2002
			US 2003082454 A1	01-05-2003
			US 6514640 B1	04-02-2003
			CA 2251709 A1	30-10-1997
			EP 0904607 A1	31-03-1999
			JP 2000509193 T	18-07-2000
			WO 9740541 A1	30-10-1997
EP 1261050	A	27-11-2002	EP 1261050 A1	27-11-2002

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/06628

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1261050	A	CA 2448175 A1	12-12-2002
		WO 02099913 A1	12-12-2002
		EP 1396038 A1	10-03-2004
		JP 2004529059 T	24-09-2004
		US 2004175614 A1	09-09-2004
<hr/>			